US Army Corps of Engineers

SEDIMENT-WATER INTERACTIONS AND CONTAMINANTS IN CORPS OF ENGINEERS RESERVOIR PROJECTS

by

Douglas Gunnison, James M. Brannon

Environmental Laboratory

DEPARTMENT OF THE ARMY
Waterways Experiment Station, Corps of Engineers
PO Box 631, Vicksburg, Mississippi 39181-0631

and

Aaron L. Mills, Linda K. Blum

Department of Environmental Sciences
University of Virginia
Charlottesville, Virginia 22903

July 1989
Final Report

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188
Exp. Date: Jun 30, 1986

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report E-89-2	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION See reverse.	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS (City, State, and ZIP Code) See reverse.	7b. ADDRESS (City, State, and ZIP Code)

8a. NAME OF FUNDING/SPONSORING ORGANIZATION US Army Corps of Engineers	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code)

Washington, DC 20314-1000

10. SOURCE OF FUNDING NUMBERS			
PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
			32513

11. TITLE (Include Security Classification)

Sediment-Water Interactions and Contaminants in Corps of Engineers Reservoir Projects

12. PERSONAL AUTHOR(S)

Gunnison, Douglas; Brannon, James M.; Mills, Aaron L.; Blum, Linda K.

13a. TYPE OF REPORT Final report	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) July 1989	15. PAGE COUNT 51

16. SUPPLEMENTARY NOTATION

Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Adsorption Hydrodynamics Sediment
			Contaminant Microbial degradation
			Desorption Reservoir

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Contaminants in Corps of Engineers (CE) reservoir and waterway projects have caused problems in the past. The potential for these contaminants to cause additional problems has increased as more sophisticated water quality sampling programs and analyses have been adopted by field offices. Contaminant-sediment-water interactions are major mechanisms determining contaminant levels in project waters and availability of contaminants for biological uptake. This report examines the literature on sediment-water interactions and contaminant processes with respect to the unique conditions present in reservoirs. The report also examines the results of CE District surveys conducted to determine the nature and magnitude of contaminant problems in reservoir projects. Recommendations for future investigations are made based on the frequency of contaminant occurrence in CE projects and the major mechanisms for contaminant interactions with sediment and water.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

6a. NAME OF PERFORMING ORGANIZATION (Continued).

USAEWES, Environmental Laboratory;
University of Viginia, Department of Environmental Sciences

6c. ADDRESS (Continued).

PO Box 631, Vicksburg, MS 39181-0631;
Charlottesville, VA 22903

PREFACE

This report presents a literature survey of sediment-water-contaminant interactions in natural waters. This information is then integrated with the results of several surveys conducted to assess specific problems with contaminants determined in Corps of Engineers reservoirs. The work was sponsored by the Water Quality Research Program (WQRP) Work Unit 32513, "Sediment-Water Interactions and Contaminant Processes in Reservoirs."

Funding for this study was provided by Headquarters, US Army Corps of Engineers (HQUSACE), under appropriation number 96x3121, Construction General, to the WQRP, US Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. The HQUSACE Technical Monitor of the WQRP was Mr. David P. Buelow.

The study was conducted by Drs. Douglas Gunnison and James M. Brannon of the Aquatic Processes and Effects Group (APEG), Environmental Research and Simulation Division (ERSD), Environmental Laboratory (EL), WES. Drs. Linda K. Blum and Aaron L. Mills, of the Department of Environmental Sciences, University of Virginia, Charlottesville, VA, assisted with the literature review.

The study was conducted under the direct supervision of Dr. Thomas L. Hart, APEG, and under the general supervision of Mr. Donald L. Robey, Chief, ERSD, and Dr. John Harrison, Chief, EL. Manager of the WQRP was Mr. J. Lewis Decell. The report was reviewed by Dr. Judith C. Pennington and Mr. Robert C. Gunkel, Jr., ERSD, and Dr. Winston Lung, University of Virginia. The report was edited by Ms. Lee T. Byrne of the WES Information Technology Laboratory.

COL Dwayne G. Lee, EN, was Commander and Director of WES. Dr. Robert W. Whalin was Technical Director.

1

CONTENTS

SEDIMENT-WATER INTERACTIONS AND CONTAMINANTS
IN CORPS OF ENGINEERS RESERVOIR PROJECTS

PART I: INTRODUCTION

Background

1. Contaminants in Corps of Engineers (CE) water resources projects
have often caused problems in the past and have resulted in increased costs
associated with project operation. Public awareness of environmental con-
cerns, such as potential negative influences caused by acid rain, acid mine
drainage, pesticides, etc., increases the possibility for the CE to experience
additional problems with contaminants in reservoirs and their release waters.

2. Sediment-water interactions participate directly in the mobilization
and immobilization of contaminants in rivers, lakes, and estuaries and are
influenced by the properties of the sediment, amount of contaminant associated
with the sediment, and concentration of suspended sediment in the water. The
sediment surface area and sediment properties such as redox potential, pH,
alkalinity, total organic carbon, iron, and manganese oxides are also known to
influence sediment-water interactions. However, interactions between contami-
nants and other components of the aquatic environment, including suspended and
bottom sediments during reservoir operation, are unknown. Therefore, evalua-
tion of the influence of contaminated bottom and suspended sediment on project
water quality is not possible using existing information and procedures. An
understanding of and ability to manage contaminant problems in CE projects is,
therefore, impeded.

3. For purposes of this report, the term "contaminant" is defined as
any toxic chemical substance or condition that, when present in excessive
levels, causes harm to human health and/or aquatic biota and interferes with
the use of a project. In practical terms, contaminants occur as one or more
of the following: acidity and acid mine drainage, heavy metals and sulfates,
and organic substances (organochlorine compounds: pesticides and herbicides,
polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs),
plus petroleum and petroleum products). Acid mine drainage, while not a con-
taminant itself, is a result of processes that release sulfates (which cause

3

low pH), iron, and other metals which are themselves contaminants. In the
context of this report, the term "problem" refers to any real or perceived
situation in which the presence of a contaminant or contaminants result in
curtailment of project benefits, impairment of project purposes, and/or con-
flicts with State or Federal water quality standards.

Objective

4. The purpose of this literature survey is to examine existing infor-
mation on processes linked to contaminant interactions with sediment and
water. This information, along with data on existing potential and
contaminant-related problems at CE projects, will then be used as a basis for
determining research directions to develop analytical and predictive method-
ologies for assessing the influences of contaminated sediments on CE reservoir
projects.

PART II: LITERATURE REVIEW

General

5. Many problems with contaminants in reservoirs occur when contaminants, which enter reservoirs adsorbed to sediments, are released to the reservoir water or biota through sediment-water interactions. The principal sediment-water interactions of concern in this context are adsorption/desorption reactions (movement of contaminant between sediment and water). These sediment-water interactions are difficult to describe because of the complex nature of sediment (Brannon et al. 1976) and the site-specific nature of many contaminant-sediment interactions (O'Connor and Connolly 1980). Contaminants associated with sediments range from those that are highly mobile to those that are highly immobile. According to the literature, only a small portion of the chemical constituents associated with most sediments is in a highly mobile form available for rapid desorption (Fulk, Gruber, and Wullschleger 1975; Brannon et al. 1976; DiToro et al. 1982; Karickhoff and Morris 1985). For example, a significant fraction of the total amount of many metals is part of the crystalline lattice of sediment minerals, and probably should not be considered mobile (Brannon et al. 1976; Brannon, Plumb, and Smith 1980). Reports are in conflict concerning the presence of an irreversibly adsorbed fraction of organic contaminants (Crawford and Donigan 1973; DiToro et al. 1982; Corwin and Farmer 1984; Curl and Keoleian 1984; Isaacson and Frink 1984). The so-called irreversibly adsorbed phase may actually result from the slow desorption kinetics of many organic contaminants (Karickhoff and Morris 1985), rather than true reversibility.

6. The complexity of the sediment matrix has made prediction of the adsorption/desorption behavior of contaminants associated with sediments a difficult task in the absence of empirically derived data, especially for metals. Such difficulties are increased when the properties of the water and contaminants to which sediment is exposed are considered and the possible interactions of contaminants and the biota are factored in. This review will concentrate on the literature describing sediment-water interactions, both for deposited and suspended sediment. The review will then consider selection of approaches for depicting these interactions and for factors that can affect

5

adsorption/desorption results during testing. Transport of contaminants into reservoirs has been reviewed by Khalid et al. (1983).

Contaminant Interactions at the Sediment-Water Interface

7. The importance of the sediment-water interface in the cycling of chemical constituents in reservoirs and lakes has long been recognized (Mortimer 1941, 1942). The chemical and microbiological processes underlying these interactions have been considered in detail by several authors (Ponnamperuma 1972; Yoshida 1975; Gunnison, Patrick, and Engler 1985; Ryding 1985). Basically, these processes involve the sequential microbial utilization of oxygen, nitrate, manganic manganese, ferric iron, sulfate, and carbon dioxide, respectively, as electron acceptors. Utilization of these substrates occurs in stepwise fashion, and the consumption of a given substrate cannot be initiated until the bulk of the preceding substrate has been exhausted. A decrease in the oxidation-reduction potential (Eh) accompanies the transition between the initial utilization of each new substrate. During active consumption of oxygen, the oxidation-reduction potential (Eh) remains above +400 mV. Utilization of nitrate begins at approximately +330 mV, whereas reductions of manganese and iron occur at +200 and +120 mV, respectively. Sulfate reduction occurs at +50 mV, and methanogenesis, the formation of methane from carbon dioxide and acetate, begins at approximately -150 mV.

8. Introduction of fresh supplies of exhausted substrates (oxygen or nitrate for example) to a reduced millieu can, in sufficient quantities, result in an oxidation of reduced substrates and can reset the reductive processes back up the steps to the Eh level appropriate for utilization of the fresh substrate. In addition, oxygen or nitrate is capable of chemically oxidizing reduced iron, sulfide, and, at a slow rate, reduced manganese. In the presence of low levels of dissolved oxygen, microorganisms will oxidize any of these reduced forms along with ammonium-N and methane. When not combined with a precipitating anion, the reduced forms of manganese and iron are much more soluble than their oxidized counterparts and thus can move out of the sediment into the water column.

9. Brannon, Chen, and Gunnison (1985) reported on sediment-water interactions and cycling of iron, manganese, and nutrients in reservoirs. Dissolved oxygen depletion was followed by mobilization of metals and nutrients

from sediment into the overlying water due to the processes described previously. Fluxes of ammonium-N, iron, manganese, and orthophosphate-P computed from pore water concentration profiles were lower than those measured from the overlying water, except for ammonium-N. This indicated that processes at the sediment-water interface, in addition to simple molecular diffusion, were influencing releases. Production of soluble ions may occur so near the sediment surface that it is difficult, if not impossible, to measure the gradients with sufficient resolution to calculate reliable fluxes (Sundby et al. 1986).

10. The most important parameter affecting the flux of many elements from sediments into the water column is the dissolved oxygen content of the water. Mortimer (1941, 1942) reported that chemical exchange from sediment to the overlying water may exert a measurable, but quantitatively unimportant, influence upon chemical concentrations of materials in overlying waters, as long as dissolved oxygen levels at the sediment-water interface remained above the 1- to 2-mg/ℓ level. Fillos and Molof (1972) showed that release of phosphate and ammonium from benthic deposits increased appreciably when dissolved oxygen concentrations in the overlying water fell below 1.5 mg/ℓ. Ryding (1985) closely examined internal phosphorous loadings from sediments in lakes. He observed that substantial amounts of phosphorus may be released from sediments in shallow, well-mixed lakes. The dynamics and magnitude of phosphorous release from sediment in these lakes are influenced primarily by physical factors, such as seasonal variations in water temperature and yearly trends in water renewal. He suggested that these factors induce chemical and microbiological processes that control the exchange of substances between water and sediment. Dissolved oxygen levels and decreasing levels of the redox potential in the water phase of sediment are known to markedly affect the activities of the methane-producing bacteria (Cappenberg 1974).

11. Work has also been conducted on the influence of dissolved oxygen levels on the release of trace metals from sediment. Chen et al. (1976) investigated the migration of trace metals between the interface of seawater and contaminated surficial sediment. The amounts of iron and manganese released from the sediment during a 5-month leaching period were greater when the water column was anoxic. The amounts of nickel, cadmium, copper, lead, and zinc released were greater when the overlying water was aerobic. Chen et al. (1976) concluded that the direction of trace-metal migration was controlled mainly by the chemistry of the immediately overlying water and of

the interstitial water rather than by the type of sediment. The principal chemical factors were the levels of dissolved oxygen and sulfides present (Chen et al. 1976).

12. Results of more recent studies have substantiated these findings. Sundby et al. (1986) found that the critical variable controlling the reactions at the sediment-water interface is the flux of oxygen from the water column into the sediment. Decreases in dissolved oxygen in the overlying water column resulted in releases of the redox-sensitive species cobalt, iron, manganese, and phosphate from the sediment (Sundby et al. 1986). Westerlund et al. (1986) investigated fluxes of the trace metals cadmium, copper, lead, nickel, and zinc across the sediment-water interface. They found no correspondence between fluxes calculated from pore water profiles and those actually measured. However, while oxygen concentration in the overlying water decreased, the metal fluxes decreased as well and were ultimately reversed as sulfide began to appear in the water.

13. Little work has been done in the area of organic contaminant release from deposited sediments. Pritchard et al. (1986) studied the movement of kepone from water into sediment. Most kepone accumulated in the top 0.6 to 1.5 cm of sediment. Faster rates of apparent kepone diffusion from the water into the sediment were measured in the upper sediment layers. McElroy et al. (1987) reported similar results for C-14 labelled benz(a)anthracene added to the water column near the sediment-water interface. Following 42 days of incubation, 97 percent of recovered radioactivity was found in the upper 2 cm of sediment. There is no information on the effect of dissolved oxygen concentrations in the overlying water on the release of organic contaminants from sediment. However, it is likely that dissolved oxygen levels in the overlying water will not be as important in the release of organic compounds as it is for metals. Oxygen combines with many metals to form insoluble oxides.

Microbial influences on contaminants

14. Little work has been done on the influence of microbial processes on complexation and/or transformation of contaminants in sediment and how these processes influence contaminant mobility. Microorganisms are known to exert a variety of influences on various contaminants, both inorganic and organic. In the case of metals, for example, microbial activities lead to mobilization of iron and manganese (as described previously); to methylation

8

of arsenic (Braman and Foreback 1973), mercury, cadmium, lead, tin (Summers and Silver 1978), selenium (Francis, Duxbury, and Alexander 1974; Doran and Alexander 1977) and tellurium (Fleming and Alexander 1972), or chelation (primarily interactions between humic acids and metals (Mantoura, Dickson, and Riley 1978)).

15. Microorganisms also participate in a variety of reactions that transform organic contaminants, and some of these transformations result in an increase in mobility and/or toxicity of contaminants. Alexander (1977) listed these reactions in detail; some are especially relevant to microbial activities with contaminants in sediment. Among the most important are the following:

a. Degradation reactions involving conversion of substrates from complex forms into simpler products, with the products often being more mobile and sometimes more toxic than the original substate.

b. Conjugation, complex formation, or addition reactions involving conversion of substrates into more complex forms, reactions that may substantially alter substrate mobility, usually through increases in solubility.

c. Activation reactions involving conversion of nontoxic substrates into toxic forms.

d. Reactions changing the spectrum of activity involving transformation of a compound toxic to one group of organisms into a form toxic to another group of organisms.

16. Degradation reactions are important when considering those organic contaminants that persist in the environment. Microbial degradation influences the availability of organic contaminants to various portions of the environment by decreasing the supply. For example, degradation of PAHs is carried out by several different kinds of microorganisms (Cerniglia and Gibson 1978; Kiyohara and Nagao 1978; Cerniglia, Gibson, and Van Baalen 1980; Ensley, Gibson, and Laborde 1982; Schocken and Gibson 1984). However, the degradation process apparently requires the presence of dissolved oxygen or nitrate (Mihelcic and Luthy 1988a). Microbial degradation may also be dependent on PAH sorption-desorption reactions with soil and sediment and on the function of the associated organic carbon as a sorbent (Mihelcic and Luthy 1988b). The highest concentrations of PAHs often occur in surficial sediments (Eadie et al. 1982), and microbial degradation of PAHs is between 8 and 20 times higher in sediment than in natural waters (Hallett and Brecher 1984).

In either location, PAH degradation rates are slow (Hallett and Brecher 1984), and PAHs persist longer in reduced sediments than in the oxidized surface sediment layers (DeLaune, Patrick, and Casselman 1981). In addition, naturally occurring organic carbon may, if bioavailable, serve as the dominant source of organic carbon for use in microbial reactions, limiting microbial degradation of a given contaminant (Mihelcic and Luthy 1988b). However, the same organic carbon may have the opposite effect on cometabolism of contaminants. Other compounds, such as PCBs are difficult to degrade under either aerobic or anaerobic conditions, owing in large part to steric hindrances caused by their chlorine substituents (Furukawa 1982). It is important that dechlorination, which makes PCBs less toxic, usually can occur under aerobic and anaerobic conditions. Brink (1983) has indicated that microorganisms able to degrade most of the chlorinated biphenyls present in commercial PCB products occur in many areas of the environment. The PCBs having fewer chlorines degrade more readily under aerobic conditions (Brink 1983); however, PCBs having larger numbers of chlorine substituents are more readily degraded under anaerobic conditions (Brown et al. 1987).

Methods for assessing contaminant release

17. Methods for describing the release of contaminants from sediment into the overlying water include laboratory column studies (Brannon et al. 1976; Brannon, Chen, and Gunnison 1985), in situ benthic chambers (Nyffeler, Santschi, and Li 1986), diffusion calculations based on pore water gradients (Lerman 1979; Brannon, Chen, and Gunnison 1985), and equilibrium partitioning calculations for hydrophobic organic contaminants coupled with a diffusion model (Brannon et al. 1989). Of particular interest is a review by Reuber et al. (1987) of the kinetic and equilibrium processes influencing the behavior of organic contaminants in the vicinity of the sediment-water interface. They present a series of relatively simple mathematical models to illustrate some expected relationships between water, sediment, and biota. Such approaches, in conjunction with methods previously referenced, are a useful starting point for describing release of trace metals and organic contaminants from deposited sediment.

Contaminant Interactions with Suspended Sediment

18. In the previous section, the release of contaminants from deposited sediment was considered. However, for some contaminants, interactions with suspended sediment may be of greater importance than release from deposited sediment. Suspended sediment in reservoirs may originate from deposited sediment (Ross, Nriagu, and Wong 1983) or from point and nonpoint sources. Resuspension of deposited sediment is strongly dependent on the height of the water column and the energy regime (Ross, Nriagu, and Wong 1983). Inputs of suspended sediment from point and nonpoint sources are greatest following storm events (Gunkel et al. 1984), but are always present in some amount in a reservoir system.

19. The following information on sorption of organic and metal contaminants to suspended particles is derived from an unpublished contract report by Blum and Mills.* This report describes the role of microorganisms in the production of dissolved organic matter and mobilization of contaminants in dissolved organic form.

Sorption of Organic Contaminants

Inorganic particles

20. Sorption of organic matter to inorganic particles is important for two reasons. First, if the material sorbed is an organic contaminant, the interaction can remove the contaminant from the water column. Sorption reactions can be either ionic (see below) or hydrophobic. Sorption of a contaminant to a clay particle is important because the material is likely to settle and be buried, and it may be permanently removed from the water column. Second, dissolved organic matter is often sorbed to organic contaminants and can contribute greatly to interactions with the particle. An organic coating can tightly bind metals to inorganic particles (Davis 1984). Other investigators have found that trends in metal sorption to surficial sediments in the ocean

---

* L. H. Blum and A. L. Mills, 1986, "Evaluation of the Literature on the Role of Microorganisms in Production of Dissolved Organic Matter and Mobilization of Contaminants in Dissolved Organic Matter Form from Flooded Soils and Sediments," unpublished report, Department of Environmental Sciences, University of Virginia, Charlottesville, VA.

were not related to the apparent stability constants determined for clean inorganic surfaces; however, the trends were better correlated with the complexation properties of marine humics (Balistrieri, Brewer, and Murray 1981).

Particulate and
dissolved organic compounds

21. Dissolved organic matter can have many effects on contaminants, but as indicated previously, this material also sorbs readily to inorganic particles. To clarify possible interactions between inorganic particles coated with organic matter, it is important to consider dissolved organic matter-organic contaminant interactions both in solution and in combination with particles.

22. Dissolved organic matter present in aquatic ecosystems can influence the physical state and environmental fate of organic contaminants. Humic substances are a major form of dissolved organic matter. Humics exert their influences through: (a) increasing the apparent water solubility of nonpolar compounds (Wershaw, Burcar, and Goldberg 1969; Ogner and Schnitzer 1970a, 1970b; Ballard 1971; Boehm and Quinn 1973; Matsuda and Schnitzer 1973; Mathur and Morely 1978; Hassett and Anderson 1979, 1982; Landrum et al. 1984); (b) binding organic compounds through covalent bonds, charge-transfer complexes, hydrogen bonding, or Van der Waals interactions (Paris, Wolfe, and Steen 1982; Perdue 1985); (c) hydrolyzing pesticides (Perdue 1983); (d) photosensitizing contaminants (Zepp, Baughman, and Schlotzhauer 1981a, 1981b); (e) altering bioavailability of contaminants to aquatic organisms (Leversee et al. 1983); and (f) controlling the rate and extent of biodegradation of organic contaminants at low concentrations (Novick and Alexander 1965, Holm et al. 1980, Schmidt and Alexander 1985).

23. Wershaw, Burear, and Goldberg (1969) have demonstrated the ability of dissolved organic matter to increase the apparent aqueous solubility of hydrophobic organic compounds. A 0.5-percent humic acid solution increased the apparent solubility of dichlorodiphenyltrichloroethane (DDT) a minimum of twentyfold over that of DDT in water alone. Addition of sodium chloride at levels of 0.1 to 1.0 percent did not influence DDT solubilization, suggesting that ionic interactions with the dissolved organic matter were not responsible for the solubilization. Humic acids also sorbed the water-soluble herbicide 2,4,5-T. Fulvic acid has been shown to interact with and solubilize hydrophobic dialkyl phthalates (Matsuda and Schnitzer 1973). The solubility of

certain alkanes (hexadecane, eicosane, pristane) is also influenced by fulvic acid, although the latter substance does not appear to influence the solubility of some aromatic hydrocarbons (phenanthrene and anthracene) (Boehm and Quinn 1973). Similar positive effects on solubility have been noted between dissolved organic matter and either cholesterol or 2,2',5,5'-tetrachlorobiphenyl (TCB), although in this case, increasing the dissolved organic matter (DOM) concentration above certain levels decreased TCB adsorption to particles (Hassett and Anderson 1979, 1982). The latter phenomenon was ostensibly due to the formation of soluble complexes between hydrophobic compounds and DOM, as opposed to competition between DOM and TCB for adsorption sites on the particles.

24. Several studies have examined the effects of dissolved humics on the hydrolysis of organic contaminants. Atrazine (2-chloro-4-ethyamino-6-isopropylamino-s-triazine) was found to undergo hydrolysis at pH 4.0 in aqueous suspensions of humic acid and acetic acid, possibly as a result of a catalytic effect of humic acid (Li and Felbeck 1972a, 1972b). Aqueous solutions of fulvic acid are also able to catalyze atrazine hydrolysis (Khan 1978a). Humic substances have been found to accelerate hydrolysis rates of several alkyl esters of 2,4-D at pH 7.65 (0.0066 M phosphate buffer). In contrast, Perdue and Wolf (1984) found that humic acid solutions of pH 9 to 10 substantially decreased the hydrolysis rate of the 1-octyl ester of 2,4-dichlorophenoxyacetic acid. Such variable results for the hydrolysis of hydrophobic organic contaminants have been explained in a kinetic model developed by Perdue (1983). This model, based on analogy with the effects of anionic detergent micelles on hydrolysis kinetics, includes equilibrium partitioning (see paragraphs 32-37), general and specific acid-base catalysis, and surface micellar catalysis. Perdue used studies by Li and Felbeck (1972a, 1972b) and Perdue and Wolf (1984) to test the model. The results indicated that humic substances may alter reactivities for bound substates; base-catalyzed reactions should be inhibited whereas acid-catalyzed reactions should be accelerated. Perdue (1983) concluded that reactions susceptible to both acid and base catalysis in aqueous solutions will be retarded by humic substances in base solution, but accelerated by humic substances in acid solution. Thus, such reactions are expected to be accelerated in reservoir projects in which impounding waters containing humic materials are also subject to acid rain and/or acid mine drainage.

13

25. Several studies have indicated that certain chemicals photolyze more rapidly in natural water samples than in distilled water (Ross and Crosby 1975; Zepp et al. 1975, 1977; Zepp, Baughman, and Schlotzhauer 1981a, 1981b; Mills et al. 1982). For example, disulfoton and 2,5-dimethylfuran, aniline, and cis-1,3-pentadiene are photosensitized in the presence of humic and fulvic acids (Zepp, Baughman, and Schlotzhauer 1981a, 1981b). At low dimethylfuran, concentrations reactions are first order, and the reactions rate constants are directly proportional to both the average light intensity and the concentration of humic substance. The rate of photosensitization of dimethylfuran induced by humic substances is pH independent in the range of 5 to 9 and requires radiation in the ultraviolet or blue range.

26. A few studies examine the effect of DOM (especially humics) on the bioavailability of organic contaminants in aquatic organisms (Crosby and Tucker 1971; Boehm and Quinn 1973; Neely, Branson, and Blau 1974; Southworth, Beauchamp, and Schneider 1978; Leversee et al. 1981, 1983). These studies suggest that humic acids have complex effects on the bioavailability of PAHs. Leversee et al. (1983) compared the effects of natural and synthetic DOM on bioavailability of several PAHs (naphthalene; anthracene; benzo[a]pyrene; 1,2,5,6-dibenzanthracene; 7,12-dimethylbenzo[a]anthracene; and 3-methylcholanthrene) at different DOM and PAH concentrations. The results indicated that humics reduce the partitioning of single unsubstituted PAH into *Daphnia*, with the greatest reduction observed for PAHs having the largest octanol-water partitioning coefficient (benzo[a]pyrene > anthracene < naphthalene). The accumulation of methylcholanthrene in *Daphnia* was increased in the presence of humics, although the exact manner was unclear.

Sorption of Metals

27. Metals tend to sorb to particles or complex with organic matter through ion exchange-related mechanisms; however, many organometallic complexes occur through covalent bonds. Covalent bonds are normally more stable than ionic bonds, but ion exchange is the most common form of metal sorption to inorganic surfaces.

Inorganic particle surfaces

28. The presence of O and OH groups on the crystal surface of clays and other organic particles gives these materials a net negative surface charge.

14

This negative charge can be augmented through inclusions of cations other than aluminum or silicon in the interior of the clay lattice (isomorphous substitution). The charge results from an acid-type of dissociation whereby

$$Lattice-OH \longleftrightarrow Lattice-O- + H+$$
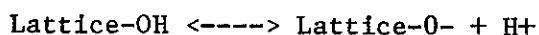
The equilibrium is such that at low pH (pH << pKa), the negative charge is saturated with protons, leaving no negative charge to attract other cations. At pH >> pKa , the supply of protons is very small, resulting in a negative charge that is then available to attract other cations, i.e., metals. At pH values near the pKa (approximately ±1.5-pH units), the supply of negative charge for exchange of ions will be controlled by the proton supply, and the charge is pH dependent. This means that in low pH environments such as acid mine drainage and acid rain-influenced reservoirs, metals are more mobile because of displacement of metals from clay surfaces by the abundant protons in the water. However, recent literature shows that particles may have positive charges in water affected by acid mine drainage (Newton and Liss 1987). In higher pH environments, metals are more tightly held because of the lack of protons for displacement.

29. Davis (1982) demonstrated that much of the surface area on most inorganic particles is coated with organics sorbed from DOM. The organic coating can have various roles, according to the ambient pH, the amount of surface area on the particle, the amount of adsorbable organic matter present, the nature of the solid portion of the particle, and the inorganic electrolyte composition. The mechanisms through which dissolved organics can act to enhance the adsorption of cations involve increasing the effective number of negatively charged sites on a particle. However, Davis also indicated that adsorption of organic matter to inorganic particles inhibited the sorption of anions to the surface (i.e., phosphate).

Organic particle surface

30. In like manner to inorganic particle sorption, the sorption of metals to organic particles results primarily from ionic reactions. Here, the primary active sites on the particles are carboxylic acids and phenols (Schnitzer and Khan 1972). These groups are also extremely important in interactions involving dissolved organic substances. The negative charge occurs according to the following reactions:

15

$$R\text{-COOH} \longleftrightarrow R\text{-COO-} + H+$$

$$R\text{-OH} \longleftrightarrow R\text{-O-} + H+$$
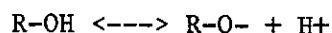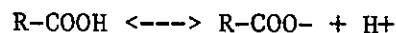
where

R-COOH = a carboxylic acid

R-OH   = a phenol

These reactions are also pH-dependent, as was the case for the clay, and the specific pH ranges where the pH dependency will be exerted depends on the pKa for the functional group involved. A critical microbial role in this area is the mineralization of particulate organic matter in the particles or sediments to form DOM with exposed phenolic and carboxylic acid groups.

Contaminant Distributions Between Suspended Sediment and Water

31. Different methods have been used to describe contaminant distribution between suspended sediment and water in natural aquatic systems. However, all of the methods used are variations of either equilibrium or nonequilibrium approaches. Equilibrium processes are controlled by thermodynamics and may involve mass transfer, whereas nonequilibrium processes involve reaction kinetics and mass transfer (Bird, Stewart, and Lightfoot 1960; Thibodeaux 1979; Geankoplis 1983). Consequently, it may be necessary to involve all three areas (thermodynamics, reaction kinetics, and mass transfer) to describe suspended sediment-water interactions in CE water resources projects.

Adsorption/Desorption Equilibrium Processes

Distribution
(partitioning) coefficient

32. Adsorption processes have been studied for many years and form the basis upon which adsorption/desorption theory has developed. Equilibrium processes are easily described mathematically, and chemical measurements for such processes are easier to quantify analytically than are those for nonequilibrium processes in a sediment-water system. Factors such as the rate of attainment of equilibrium conditions and the residence time of suspended sediment in the water column greatly influence the choice of predictive

16

approaches. However, for some reservoir contaminant problems and situations, it is possible that equilibrium distribution coefficients may describe contaminant adsorption/desorption behavior adequately for modeling purposes.

33. For the present discussion, the sediment-water interface is defined as the place at which the solid phase and the aqueous phase meet and interact. In the previous sections, this was at the interface between water and deposited sediment or between water and the surface of the suspended particle. A contaminant introduced on one side of the interface will move across the interface until equilibrium is established. At equilibrium, the contaminant is distributed or partitioned between the two phases so that the chemical potentials in the solid and aqueous phases are equal (Thibodeaux 1979). Equilibrium considerations for suspended sediment leaching involve interphase equilibria for gas, aqueous, and solid phases.

34. For suspended sediments in reservoirs, only one equilibrium, sediment/water, must be considered. If the rate of contaminant transfer across the sediment particle/water interface is rapid relative to convective and dispersive transport, then for all practical purposes, chemical equilibrium exists between water and sediment particles. In this case, the adsorption/desorption process will be equilibrium controlled, and distribution coefficients can be used to describe interactions between suspended sediment and contaminants.

35. Derivation of distribution coefficients between sediment and water based on aqueous- and solid-phase fugacities can be found in Hill, Myers, and Brannon (1988). Such distribution coefficients can be expressed in terms of concentration as follows:

$$q = Kd \; C \tag{1}$$

where

     q = solid-phase contaminant concentration, mg/kg

   Kd = distribution coefficient, ℓ/kg

    C = aqueous-phase contaminant concentration, mg/ℓ

This relationship holds if the following conditions are satisfied:

    <u>a</u>. The suspended sediment-water system approaches steady state.

    <u>b</u>. The solid-phase contaminant concentration is much less than the ultimate adsorption capacity of the sediment.

17

    <u>c</u>. The aqueous-phase contaminant concentration is not solubility limited (i.e., does not precipitate).

    <u>d</u>. The gas phase is insignificant.

36. In general, Kd is not constant unless the ratio of the solid- and aqueous-phase fugacity (product) is constant. If the phase reference fugacities are constant, Kd varies with changes in the chemical activity coefficient, oxidation-reduction potential (Eh), and possibly other factors related to aqueous-phase chemical potentials. The solid-phase activity coefficients depend primarily on Eh and the geochemistry of the suspended sediments. Hence, Kd is a true constant only if the fugacities of the solid and aqueous phases remain in constant ratio.

37. Geochemical processes in the solid phase are relatively slow compared with those in water. For this reason, the solid-phase fugacity is less variable than the aqueous-phase fugacity. Karickhoff (1984) has reported evidence that the solid-phase fugacity (product) is reasonably constant for hydrophobic organic chemicals. If this is true, Kd for hydrophobic organic chemicals will be primarily a function of the affinity of the compound for water. Karickhoff was able to correlate Kd to the water-octanol partition coefficient Koc.

Adsorption isotherm equations

38. The adsorption process involves the association and preference of a sorbate for a solid substance. Adsorption can be defined as a combination of elementary processes involved in the removal of materials from solution. While processes such as reversible and irreversible chemical reactions, physical entrapment, and precipitation are involved in adsorption, it is advantageous to consider these as a single process. However, on the theoretical level and for explaining observed phenomena, the various mechanisms should be recognized.

39. Adsorption isotherms have been used to define the equilibrium distribution of sorbate molecules between the solid phase and the aqueous phase (Weber 1972). Adsorption isotherms are determined by contacting varying quantities of sorbent with aliquots of fluid containing the sorbate. At equilibrium, each sample will have a different aqueous-phase concentration and a different sorbed concentration. Consequently, a table of values may be generated for the mass of sorbate per mass of sorbent, q, versus the

18

aqueous-phase concentration, C . If the table values are plotted, a curve
similar to Figure 1 is usually obtained. This figure shows that the sorbent
loading asymptotically approaches a limiting value as aqueous-phase concentra-
tions become large.

40. The Freundlich and Langmuir equations have been used to model the
curve shown in Figure 1 (Weber 1972). The mathematical forms of the two equa-
tions differ as a result of differences in the kinetics that are modeled by
the two equations. These differences are discussed in Hill, Myers, and
Brannon (1988). The Freundlich and Langmuir adsorption equations are pre-
sented as Equations 2 and 3, respectively.

$$q = KC^{1/n} \tag{2}$$

where

       q = contaminant mass concentration in solid phase

$K, 1/n$ = Freundlich coefficients

      C = mass concentration of a selected contaminant in aqueous phase

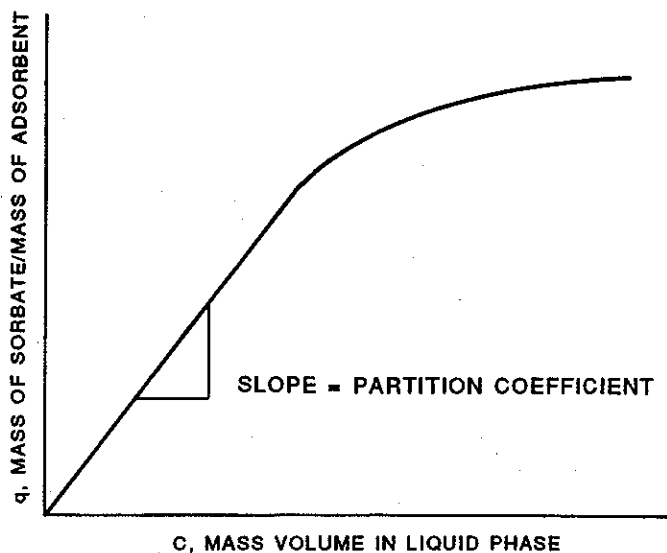$$q = \frac{KQoC}{1 + KC} \tag{3}$$

Figure 1. Adsorption-desorption curve
modified from Weber (1972)

19

In Equation 3, K is the Langmuir coefficient related to entropy, and Qo is the ultimate adsorbent capacity (monolayer) of the sorbent.

41. The Freundlich and Langmuir equations model the nonlinear region of the adsorption isotherm as well as the linear. In the linear region of the adsorption isotherm where the adsorbed concentration is far below the adsorption capacity of the sorbent, a single distribution coefficient such as Equation 1 can be used to relate aqueous-phase concentrations to adsorbed phase concentration.

Desorption isotherms

42. Desorption isotherms are obtained by sequential batch leaching of contaminated sediment. When steady state is reached, the sorbed and aqueous phases are separated and analyzed. The sediment is then challenged by a new (clean) aliquot of leaching medium until equilibrium is again reached. By repeating this procedure, a table of values can be generated for the mass of contaminant per mass of sediment, q , versus the aqueous-phase concentration, C . If the table of values is plotted, a desorption isotherm will result. Like the adsorption isotherm, the desorption isotherm describes an equilibrium-controlled process.

43. If adsorption- and desorption-dominated processes occur under constant conditions, the desorption of a contaminant back into the aqueous phase should exactly follow the adsorption curve. For this to occur, adsorption must be completely reversible, and identical sorption processes must take place during desorption as took place during adsorption. Laboratory adsorption and subsequent desorption experiments by several investigators (Mustafa and Gamer 1972, DiToro and Horzempa 1982, Corwin and Farmer 1984) have shown that adsorption and desorption processes are typically not identical. The behavioral differences of contaminants during adsorption and desorption processes are referred to as hysteresis. From a modeling standpoint, this means that specific adsorption and desorption isotherms are required. Linear desorption isotherms can be modeled using Equation 1.

44. A term for a strongly or irreversibly absorbed fraction, qr , can be added to the Freundlich equation as follows:

$$q - qr = KdC \qquad (4)$$

45. Equation 4 models linear desorption processes. However, not all sorption processes are linear. For the process to be linear, the experimentally determined coefficients, Kd and qr , must be independent of C and q as well as of solubility and adsorption limits. Equations 1 and 4 apply if the solid-phase concentration, q , is much less than the ultimate adsorption capacity of the sediment and if the aqueous-phase concentration is not solubility limited. If either phase is approaching its capacity to contain a contaminant(s) or if Kd is not independent of C and q , the isotherm will be nonlinear. A solid-phase concentration dependency for distribution coefficients has been reported by several investigators (Houle and Long 1980; O'Connor and Connolly 1980; DiToro et al. 1982; Voice, Rice, and Weber 1983). With the aid of existing computer programs, nonlinear isotherms may also be used to model equilibrium-controlled desorption.

Nonequilibrium Processes

46. Nonequilibrium adsorption/desorption processes have been examined in detail by Hill, Myers, and Brannon (1988). The brief summary presented in this report addresses the most important aspects of nonequilibrium processes. One of its most important aspects is a potential toward change when such nonequilibrium conditions exist. Rate processes therefore become important in describing the system's approach to equilibrium. Use of rate processes to describe sediment-water interactions is generally much more complex than use of an equilibrium approach because use of rate processes requires knowledge of the elementary reaction pathways and their rate constants (Nyffeler, Li, and Santschi 1984). Therefore, modeling of the time-dependent distribution of contaminants into water and sediment is generally empirical in nature because such an approach summarizes the complex interactions of dissolved and particulate forms of the contaminants (Nyffeler, Santschi, and Li 1986). For a more rigorous investigation of trace-element cycling, trace-element speciation and an understanding of all reactions of the dissolved element with the solid phase and its surface would be necessary (Nyffeler, Santschi, and Li 1986). Such an approach is beyond present capabilities.

47. The overall rate of exchange between the particle and water may be controlled by one of several processes. These include external diffusion through a film, internal diffusion within the intersections of the sediment

solid phase, or reaction kinetics at the sediment-water interface (Weber 1972). Generally, rate processes are controlled by mass transfer, rather than the kinetics of chemical reactions.

48. Mass transfer can control the overall rate of desorption in the following four ways: (a) nonsteady-state diffusion through a stagnant layer of water immediately adjacent to the external surface of each sediment particle; (b) intraparticle, aqueous-phase diffusion from desorption sites within the porous structure of the sediment particle; (c) solid-phase diffusion to the pore walls; and (d) solid-phase diffusion along pore walls. Nonsteady-state diffusion through a stagnant layer of water immediately adjacent to the external surface of each sediment particle is an important mechanism in some systems (Bird, Stewart, and Lightfoot 1960; Weber 1972; Rao et al. 1979). It assumes that the rate of desorption is controlled entirely by the rate of contaminant diffusion (mass transfer) across a laminar film that separates the sediment surface and the bulk of the aqueous phase. Relationships have been developed that can be used to estimate a film mass transfer equation (Hill, Myers, and Brannon 1988). Mixing of water and sediment such as that employed in a laboratory batch test tends to reduce the boundary layer thickness. When this happens, the bulk aqueous concentration approaches the equilibrium concentrations at the sediment surface.

49. Mass transfer can also be controlled by intraparticle, aqueous-phase diffusion from desorption sites within the porous structure of the sediment particle to the exterior. Wu and Gschwend (1986) support the theory that the sorption kinetics of hydrophobic organic compounds is controlled by intraparticle diffusion for natural aggregated sediments and soils. Aqueous-phase diffusion may be the primary route of internal contaminant mass transfer, but other mass transport processes such as solid-phase diffusion to the pore walls and solid-phase diffusion along the pore walls may also occur (Weber 1972). Combined internal (solid- and aqueous-phase) diffusion and external diffusion (film) may also occur (Weber 1972). These processes are usually very slow in comparison to other processes, and in many circumstances they can be ignored. If ignored, the implied assumption is that contaminants in the internal pores are not leachable.

50. Mass transfer considerations are important when sediment-water interactions are studied, but chemical kinetics may also be important under certain conditions. Chemical kinetics can be rate limiting when they limit

22

the transfer of material between phases at the particle surface. When reaction rates of processes, such as dissolution of minerals or precipitation of low-solubility salts, are such that equilibrium is attained very slowly (if ever), then the kinetics of the reactions are rate controlling. A summary of equations for equilibrium and nonequilibrium approaches to adsorption/desorption are summarized in Hill, Myers, and Brannon (1988).

51. Other approaches to describing contaminant-suspended material interactions on a kinetic basis may also be applicable. Nyffeler, Santschi, and Li (1986) described a numerical transport model that is based on sorption kinetics and includes time-dependent parameters such as particle settling velocity, concentration or flux of particles, and depth-dependent variables in sediments such as bioturbation rates and porosity. The model was designed to be used as a subroutine of a comprehensive transport model of a lake or parts of the ocean (Nyffeler, Santschi, and Li 1986). The model has been used to simulate removal of radiotracers from the water of enclosed shallow aquatic systems, penetration of tracers into sediment, and the remobilization of tracers from sediment.

Selection of an Equilibrium or Nonequilibrium Approach

52. Selection of the proper approach to use in describing sediment-water interactions is difficult. Several models are available that assume equilibrium (often instantaneous) between dissolved and particulate phases (Whitfield and Turner 1979; Li 1981; Schnoor 1981, 1985; Bacon and Anderson 1982; Balistrieri and Murray 1983; O'Connor 1988a, 1988b, 1988c). Coefficients for use in these models were obtained by direct measurement, batch testing, or assumptions. Once determined, equilibrium values are assumed to remain constant for similar conditions regardless of reaction time relative to particle residence time (Jannasch et al. 1988). Equilibrium models were used because trace metal uptake by suspended particulates was assumed to be rapid. This assumption was based on the theory that adsorption consisted of very rapid (seconds to minutes) specific adsorption (Stumm, Huang, and Jenkins 1970). Adsorption of trace metals does occur rapidly in systems where pure metal oxides are the sorbent (Hachlya et al. 1979, Hayes and Leckie 1986). Therefore, until recently, trace metal uptake rates have been assumed to be rapid and unimportant. Studies (Li et al. 1984; Nyffeler, Li, and Santschi

23

1984; Balistrieri and Murray 1986; Santschi et al. 1986) of radiotracer uptake by natural sediments have shown much slower kinetics than measured for pure metal oxides. Adsorption, often requiring weeks to reach equilibrium, suggests that physical, chemical, or biological processes other than coordination reactions are involved in adsorption.

53. Various studies (Nyffeler, Li, and Santschi 1984; Santschi 1984; Santschi et al. 1986; Jannasch et al. 1988) indicate that an equilibrium approach may not be valid for locations with high particle turnover rates, such as reservoirs. Nyffeler, Li, and Santschi (1984), using Narragansett Bay sediments, demonstrated that sediment-water interactions for zinc, selenium, strontium, cadmium, tin, antimony, cesium, barium, mercury, thorium, and palladium reached a constant distribution ratio after a few days of equilibration. Beryllium, manganese, iron, and cobalt showed increasing distribution ratios over the whole period of equilibration (108 days). Jannasch et al. (1988) reported that metals with the highest final distribution coefficients sorb much more rapidly in the initial stages (minutes). More weakly bound metals, such as zinc, are taken up much more slowly (within days). Weakly associated metals did not approach equilibrium during the measured period (10 days). For tin, approximately 95 percent of sorption was completed within 1 min. Therefore, an equilibrium adsorption model could prove adequate (Jannasch et al. 1988) for tin. Desorption coefficients were found to vary by only about a single order of magnitude (Jannasch et al. 1988), leading the authors to speculate that the desorption process is physical and independent of the metals involved.

54. DiToro and Horzempa (1982) reported that the adsorption process was rapid (minutes to hours) for hexachlorobiphenyl, but that the reverse process, desorption, was slow because a significant portion of the sorbed chemical was resistant to release. Karickhoff (1980) reported similar kinetic factoring for both adsorption and desorption of PAHs in natural sediments. From 35 to 60 percent of the equilibrium sorption was achieved in minutes, with apparent equilibrium reached in a few hours. These results may be due to analytical limitations, because for some systems where sufficient analytical accuracy could be achieved, sorption continued to change (increase for adsorption, decrease for desorption) over periods of days to weeks. Karickhoff and Morris (1985), using more sensitive experimental techniques, reported that true sorption equilibrium required, in some cases, days to weeks to achieve for

hexachlorobenzene, pentachlorobenzene, pyrene, and trifluralin. The kinetic exchange constant for nonlabile sorption varied inversely with the sorption equilibrium constant. That is, the more highly sorbed chemicals sorbed more slowly (Karickhoff and Morris 1985).

55. Kinetic studies for metals and organic contaminants have demonstrated that different elements and compounds approach equilibrium at different rates, a factor that can greatly influence the choice of a predictive approach. However, the kinetics of the interaction between contaminants and sediment are not the sole concern when a predictive approach for describing sediment-water interactions is selected. Estimation of particle residence time in reservoirs is necessary to determine the extent of the sorption process and the potential of equilibrium models to sufficiently describe sediment-water interactions (Santschi 1984; Nyffeler, Santschi, and Li 1986; Santschi et al. 1986; Jannasch et al. 1988). In areas of rapid particle removal, residence times may not be long enough to allow sorption reactions to reach equilibrium (Jannasch et al. 1988). Residence time of particles is, therefore, a master variable in contaminant-water interactions, especially in environments where contaminant reaction times with particles are greater than or equal to particle residence time (Jannasch et al. 1988).

56. The optimum approach for selection of predictive methodologies for suspended sediment and water soluble contaminant interactions in CE reservoirs will, therefore, depend on the adsorption/desorption kinetics of contaminants of concern compared with the residence time of suspended sediment in the water column (Nyffeler, Li, and Santschi 1984). An equilibrium approach may be appropriate if the great majority of adsorption/desorption occurs in a short period relative to the residence time of suspended sediment in the water column. A kinetic approach is basically more appropriate to describe a system if input of either contaminants or suspended sediment is changing rapidly (Nyffeler, Li, and Santschi 1984).

Factors Affecting Sediment/Water Interactions

57. Selection of equilibrium or nonequilibrium modeling approaches will greatly influence laboratory and field testing required to obtain the proper information for describing the processes controlling contaminant interactions. However, in addition to different test procedures needed to acquire

25

equilibrium distribution coefficients or kinetic rate coefficients, experimental condtions must be carefully selected. Factors such as oxidation-reduction potential, pH, dissolved oxygen concentration, liquid-to-solids ratio, ionic strength, and sediment properties, as well as the nature of the contaminant being studied, can all affect the outcome of test procedures.

58. The effect of dissolved oxygen concentration on release of contaminants from sediment has been discussed previously for deposited sediment. Many of the same mechanisms affecting deposited sediments also affect the processes that occur in interactions between suspended sediment and water. The differing rates of approach to equilibrium of chemical contaminants were discussed for nonequilibrium processes. The studies reviewed indicated that contaminants exhibit a variety of adsorption/desorption behaviors, a fact that can limit generalizations about chemical behavior from one class of contaminants to another.

59. For a wide range of contaminants, equilibrium distribution coefficients have been shown to be inversely related to the solids-to-liquid ratio (O'Connor and Connolly 1980; DiToro et al. 1982; Voice, Rice, and Weber 1983). This effect was most pronounced for compounds such as DDT and cobalt that exhibit high partition coefficients. Staples and Geiselmann (1988) reported a strong dependency on particle concentration for kepone at suspended solids concentrations of 100 mg/ℓ and above. Solids concentration-dependent partitioning appears to be a function of the solids, not the compound (O'Connor and Connolly 1980). DiToro et al. (1982) suggested that particle-particle interaction is responsible for such solids-dependent partitioning. The dependency of distribution coefficients on solid-to-liquid ratios has also been explained as an experimental artifact related to incomplete phase separations (Gschwend and Wu 1985). According to this theory, nonsettling and nonfilterable microparticles are included in the chemical analysis of the aqueous phase because of inadequate phase separation. The result is an increase in the apparent aqueous phase concentration (reduction in the distribution coefficient).

60. The effect of liquid-to-solids ratio on kinetic rate coefficients has not been investigated, but mechanisms affecting equilibrium partitioning coefficients would be expected to exert some influence on kinetic rate coefficients. Jannasch et al. (1988) speculate that higher concentrations of particles may increase the rate of sorption kinetics.

61. The effects of ionic strength and pH on adsorption have been studied extensively (Garcia-Miragaya and Page 1976; Loganathan, Burau, and Fuerstenau 1977; Shuman 1977; Adams and Sanders 1984; Trefry and Metz 1984; Chang, Davis, and Kuwabara 1987; LaFlamme and Murray 1987; Neal et al. 1987). Shuman (1977) studied the adsorption of zinc by iron and aluminum hydrous oxides as influenced by aging and pH. Adsorption of zinc by both iron and aluminum hydrous oxides increased as pH increased. Trefry and Metz (1984) leached suspended particulates under varying pH regimes (pH 2.45 - 6.10) and found that the concentrations of copper, cadmium, and iron in leachate increased as pH of the leachate decreased. Adams and Sanders (1984) examined the release of zinc, copper, and nickel from four sewage sludges as a function of pH. The concentrations of metal released from the sludge to the super-natant liquid increased as pH decreased below a threshold value, which was approximately 5.8 for zinc-containing sludge, 6.3 for nickel-containing sludge, and 4.5 for copper-containing sludge. Investigations of the influence of pH on the sorption of cobalt, zinc, and cadmium by a hydrous manganese oxide showed that sorption of the metals increased as the pH increased and decreased as pH decreased (Loganathan, Burau, and Fuerstenau 1977). This is not unexpected since Gambrell, Khalid, and Patrick (1980) have shown that under controlled Eh-pH conditions, greater metal mobilization occurs under low pH conditions. No studies have been conducted on the effect of pH on adsorption/desorption of organic contaminants, although the effect would be expected to be minimal compared with metals.

62. The effect of ionic strength has also been extensively investi-gated, usually in conjunction with pH. Garcia-Miragaya and Page (1976) investigated the influence of ionic strength on sorption of trace amounts of cadmium by montmorillonite. Increasing ionic strength decreased the amount of cadmium adsorbed. LaFlamme and Murray (1987) evaluated adsorption of thorium on goethite as a function of ionic strength, pH, and carbonate alkalinity. Ionic strength did not influence thorium adsorption up to an ionic strength of 2.0, the highest level tested. As previously described for other studies, thorium adsorption decreased as pH decreased. Thorium adsorption decreased when 100-meq/ℓ carbonate alkalinity was reached, and no adsorption was observed above 300-meq/ℓ. Chang, Davis, and Kuwabara (1987) studied adsorp-tion of zinc onto synthetic colloidal titanium dioxide as a function of pH, supporting electrolyte (NaCl) concentration (0.1 to 0.002 M) and particle

27

concentration (2 to 50 mg/ℓ). Adsorption increased sharply with increasing pH over the range of 5.0 to 7.5. Adsorption was higher at the lower NaCl concentrations and decreased as the suspended titanium dioxide concentration was lowered. Studies conducted with pure clay minerals or metallic oxide phases have limited utility for predicting the effects that ionic strength and alkalinity will exert on sediment-water interactions because sediment is much more complex than such simple systems. However, these results strongly suggest that either equilibrium distribution coefficients or kinetic rate constants for a specific system be obtained under environmental conditions mirroring those at the site.

Reservoir-Watershed Interactions and Hydrodynamics of Reservoirs

63. The reservoir ecosystem was characterized by Kennedy, Thornton, and Ford (1985). Based on this article, important properties of reservoirs with regard to contaminants are summarized in the following paragraphs.

64. Reservoirs, like natural lakes, are strongly dependent on the surrounding watershed for their water supply, and the watershed is an important determinant of reservoir water quality. In most cases, a large single tributary supplies most water and material components to the reservoir. Reservoirs also have watersheds that are roughly one order of magnitude larger than natural lakes (Thornton et al. 1981); therefore, reservoirs have much greater water loads than lakes. Reservoirs are generally fed by higher order streams with the result that the loads brought in are much more likely to have undergone a high degree of processing prior to their introduction into the reservoir. Extensive processing has had an opportunity to occur only in the upstream, lower order stream reaches. Because larger streams are more likely to receive direct inputs from industrial and municipal point sources, reservoirs are also more likely to be affected by contaminants introduced by these sources. Sediment carrying capacity for large streams and rivers is high, and reservoirs receive high nutrient, organic matter, and sediment loads. Therefore, the opportunity for reservoirs to receive and retain contaminants, particularly those metals and organic compounds having a high affinity for sediment, is great.

65. Kennedy, Thornton, and Ford (1985) also described the characteristics of inflow mixing processes, material transport, and reservoir mixing.

The nature of the interface between inflowing stream and reservoir or lake water play a major role in determining the influences of water and material loads on the system. Reservoir tributaries are larger than those of natural lakes, carry higher flows, and often retain their riverine properties well into the reservoir. Density differences between tributary and reservoir waters determine where inflows are placed in the reservoir. Density differences originate with differences in dissolved and suspended solids levels and temperatures between inflow and reservoir waters. Seasonal thermal stratification within the reservoir develops because water reaches its maximum density at 4° C. Water density is lower at temperatures above and below 4° C. In the summer, waters overlying the bottom layer (at or near 4° C) increase in temperature and decrease in density towards the surface. In the winter, waters overlying the bottom layer (at or near 4° C) decrease in temperature and decrease in density towards the surface. Both thermal patterns result in a stable arrangement of reservoir waters in a pattern that resists mixing. The winter pattern can be further stabilized by the presence of an ice cover. In fall and spring in dimictic reservoirs, water temperatures are isothermal, and the waters are easily mixed by winds. Reservoir density-temperature relationships influence placement of inflows as incoming streams seek out and flow along a level in the reservoir having a density above that of the inflows. This process can have a pronounced effect on the eventual deposition of contaminants entering the project with inflows.

66. Deposition of sediments and their associated contaminants are determined by system hydrodynamics and mixing processes. Sediments may be deposited once and left or deposited and then resuspended and redeposited several times. Sediment sorting may occur once or repeatedly. While heavier sediments are typically deposited nearer the headwaters and fine sediments nearer the dam, repeated resuspension and redeposition may result in some projects having a varied deposition of sediments throughout the project. Since most contaminants become associated with sediments, the fate of the contaminant depends very much on the final location of the sediments. In addition, differences in seasonal hydrodynamics may be an important factor governing the sediment release rate of contaminants.

PART III: ASSESSMENT OF CONTAMINANTS IN CE RESERVOIRS

Methods

67. A survey was made to determine the nature and magnitude of contaminant problems presently occurring in the CE Districts and Divisions using three different procedures. The first method involved the use of specific information obtained during a survey conducted for the Water Quality Management for Reservoirs and Tailwaters Demonstration sponsored by the Water Operations Technical Support (WOTS) Program. By means of a questionnaire, CE Districts supplied information for each project (Gaugush, Gunkel, and Kennedy, in preparation). The second mechanism was an examination of the Annual Division Water Quality Reports, particularly those for the years 1985-1987. The third procedure involved direct telephone contact with each District to check information obtained by other sources and identify projects that could benefit from future research investigations in the sediment-water interactions and contaminant processes work unit.

Summary of Contaminant Problems

68. Table 1 compares the occurrence of each of the groups of contaminants as determined by the percentage of the 442 projects in the 10 Divisions experiencing problems with each contaminant (Gaugush, Gunkel, and Kennedy, in preparation). According to this information, problems with metals other than iron and manganese occurred most often, affecting an average of 33 percent of the projects. Problems with iron and manganese occurred in 25 and 24 percent of the projects, respectively. Problems with organic contaminants and with pH and acidity (resulting from acid mine drainage and acid rain) occurred about equally as often, each affecting 18 percent of the projects reported.

69. Problems with organic contaminants occurred most often in Missouri River Division (MRD), North Central Division (NCD), South Atlantic Division (SAD), Lower Mississippi Valley Division (LMVD), and Ohio River Division (ORD), and infrequently or not at all in Southwestern Division (SWD), South Pacific Division (SPD), North Pacific Division (NPD), North Atlantic Division (NAD), and New England Division (NED). Organic contaminants occurring in projects in the Midwest and Southwest apparently were primarily of agricultura

Table 1

Frequency of Occurrence of Problems with Specific Contaminant Groups*

Contaminant Group	Average Percentage of Projects**		
	With Problems	Without Problems	Not Evaluated
Metals other than iron and manganese	33	26	47
Iron	25	30	46
Manganese	24	28	48
Organics	18	28	54
pH and acidity	18	53	30

 * Based on the Water Quality Management for Reservoirs and Tailwaters
   Demonstration Survey (Gaugush, Gunkel, and Kennedy, in preparation).
** Based on total occurrences in 442 projects in 10 Divisions in the Corps of
   Engineers.

origin. Projects in the East and Ohio River Valley contained organic contaminants primarily of industrial origin. Based on information in the Annual Division Water Quality reports, the most frequently mentioned problems with organic contaminants were, in descending order of frequency, pesticides, phenols, miscellaneous toxics (probably underrated since most CE reservoirs are not routinely tested for the presence of priority pollutants), petroleum compounds (oil, grease, oil spills, etc.), PCBs, and herbicides. The herbicides (phenylureas, acylanilides, phenoxyacetates), which were cited least often, tend to be water soluble and to degrade within a reasonable period, and they apparently do not tend to bind strongly to sediment (Witkowski et al. 1987). Modern pesticides (organophosphates, dithioates, and carbamates) also fall into this category, whereas the older pesticides and their degradation products (DDT, dieldrin, and endrin) are highly persistent and of limited aqueous solubility. The miscellaneous toxics category (priority pollutants) was found in many projects in Baltimore District; however, most CE Districts have not surveyed their projects for the occurrence of these compounds. Thus, it is difficult to assess the importance of the latter category of compounds in projects on a CE-wide basis, and it is possible that this group of contaminants could be much more prevalent than indicated here.

70. Problems with metals other than iron and manganese occurred most often in MRD, NED, LMVD, NCD, NAD, ORD, SAD, SPD, and SWD, and infrequently in

NPD. Metals reported most often were cadmium, copper, mercury, and lead. Problems with excessive levels of dissolved iron and manganese affected projects most often in MRD, ORD, LMVD, SAD, SWD, SPD, NAD, and NED, but infrequently or not at all in NCD and NPD.

71. Fluctuations of pH were identified in 13 projects, while acid mine drainage was observed in 10 projects and acid rain affected 13 projects. Problems with pH fluctuations and acidity (acid mine drainage and acid rain) occurred frequently in several regions, but were found most often in the Midwest and the central eastern and New England areas. Because there is a close association between acid conditions and the mobilization of several metals, contamination problems related to pH and acidity are a large and complex issue.

PART IV: DISCUSSION

72. The literature survey presented in this report examined available information on the processes linked to contaminant interactions with sediment and water. The purpose of this study was to provide a basis for determining research directions for developing analytical and predictive methodologies to assess the influences of contaminated sediments on CE reservoir projects. The literature review described in detail the complex nature of sediment-water interactions and contaminant processes. Based on this review, it is apparent that an extensive body of information exists on the nature and importance of the processes occurring among contaminants, sediments, and water, although a complete understanding of the details of these processes is not always available. Among the areas examined in the literature survey were: (a) the behavior of contaminants at the sediment-water interface; (b) contaminant interactions with suspended sediment, including sorption of organic contaminants, sorption of metals, contaminant distribution between suspended sediment and water, and adsorption/desorption processes; (c) methods for assessing contaminant releases from sediment to water; (d) the importance of nonequilibrium processes; and (e) the influences of microorganisms on contaminant levels in sediment and water.

73. A large amount of information is available in the scientific literature on processes linked to contaminant interactions with sediment and water. However, it is also apparent that the analytical and predictive methodologies for assessing the influence of contaminated sediments in CE reservoir projects are not in a form suitable for application by CE field offices. A number of items must be addressed before the most appropriate methods to analyze and predict contaminant-sediment-water interactions can be selected and developed. These items are described in the following paragraphs.

74. As indicated by the literature survey, each contaminant possesses specific adsorption/desorption properties that may vary in accordance with the water and sediment quality characteristics of a given reservoir. Since several different contaminants may be present in the same reservoir simultaneously, large variations in adsorption/desorption kinetics may occur as the result of interactions and/or competition between contaminants. Without accurate data on the adsorption/desorption rates for the contaminants of

concern in CE reservoirs, the development of analytical and predictive method-
ologies for assessing contaminated sediment will be restricted.

75. The influence of solid-to-liquid ratios on contaminant partitioning
is a major factor determining contaminant interactions with sediment and
water. As indicated in the literature review, equilibrium sorption coeffi-
cients have been shown to be inversely related to the solid-to-liquid ratio.
However, the reasons for this change in sorption coefficients remain unclear,
although nonsettling microparticulates are the probable cause. In addition,
the effect of solid-to-liquid rations on kinetic rate coefficients has not
been determined.

76. The effect of particle composition on adsorption/desorption is an
important concern in assessing contaminated sediments. Fine particles having
large surface areas generally tend to sorb contaminants more readily than
large particles. Particles having net positive or negative surface charges
sorb contaminants having the opposite charge. Organic particles and organic
coatings on inorganic particles all influence contaminant adsorption/
desorption processes. Particles may acquire coatings of various inorganic or
organic substances that directly affect adsorption-desorptive processes during
their transit through the watershed and reservoir. The current literature
does not provide an understanding of the effect of particle composition on
contaminant adsorption and retention sufficient to evaluate contaminant-
sediment interactions.

77. Reservoir projects within the same basin may be generally similar,
but even these reservoirs can exhibit different contaminant suites, pool
hydrodynamics, and sediment physical and chemical properties. Reservoirs also
act as settling basins. Coarser, heavier particles often settle out shortly
after the transporting stream enters the project. Finer, lighter particles,
those which are more likely to bear contaminants, remain in suspension far
longer, perhaps even reaching the dam or quiet cove areas where sediment loads
are deposited. Other environmental factors, such as aerobic or anaerobic con-
ditions, acidic or basic pH levels, and various ionic strengths each affect
contaminant-sediment-water processes. Analytical and predictive methodologies
that do not include provisions for the effects of these phenomena will be of
limited use.

78. Microbial transformation reactions may influence contaminant mobil-
ization both by the processes carried out by microorganisms and the rates

at which these processes occur. For example, some rapid degradation reactions may remove contaminants from a reservoir system within a few weeks. Other degradation reactions occur slowly and can remove only minute amounts of a contaminant over a period of several years. Microbial degradation rates are largely unknown for the reservoir environment and are not presently incorporated into methodologies for assessing contaminated sediments.

79. Development of analytical and predictive methodologies cannot proceed until the factors influencing contaminant interactions with sediment and water are understood and the experimental procedures for measuring these interactions have been established. Once these interactions can be quantified, the most suitable analytical methodologies (equilibrium or nonequilibrium models or other mechanisms) for use in assessing contaminant behavior in reservoirs can be selected and developed. Finally, all of this information can be used to formulate a predictive methodology for contaminated sediments in CE reservoir projects.

PART V: CONCLUSIONS AND RECOMMENDATIONS

80.   Many CE reservoirs are experiencing problems resulting from the presence of contaminants in project waters and sediments.   Organic contaminants of concern include the older pesticides (e.g., DDT) and their degradation products, phenols, miscellaneous toxics (priority pollutants), PCBs, and petroleum hydrocarbons.   Among the metals of concern, iron and manganese occur commonly, as do cadmium, copper, lead, and mercury.   The mechanisms by which iron and manganese move from sediments into the water column in reservoirs are well-established and do not require further investigation.

81.   Acid mine drainage, pH fluctuations, and acid rain occur over wide regions of the country.   This is particularly true for reservoirs in the Midwest and Northeast, although the central South also has some problems.   However, the work required to address this area is extensive and significant enough to require research that is beyond the financial scope of the present work unit.

82.   The principal difficulty in managing problems resulting from the presence of contaminants in CE reservoirs is the lack of a suitable means to quantify contaminant movement within the project.   To accomplish this, research must be conducted to supply the field with guidance on analytical methodologies to assess contaminant interactions with sediment and water. This research should determine:

<u>a</u>.   Adsorption/desorption rates for the contaminants of concern.

<u>b</u>.   The impact of sediment concentration on equilibrium distribution coefficient and adsorption/desorption kinetics.

<u>c</u>.   The effect of particle composition on contaminant adsorption/desorption.

<u>d</u>.   The influence of site-specific conditions and environmental factors on contaminant-sediment-water interactions.

<u>e</u>.   The effect of microbial transformation reactions on the mobilization of contaminants of concern and establishment of ways to incorporate these reactions into methodologies for assessing contaminated sediments.

Once this work has been accomplished, research should be conducted to:

<u>a</u>.   Select the most appropriate analytical methodologies (models or other mechanisms) for use in describing contaminant behavior in CE reservoir projects.

36

<u>b</u>. Use the information obtained from this work for the development of predictive methodologies for Corps-wide application.

37

REFERENCES

Adams, T. M., and Sanders, J. R. 1984. "The Effects of pH on the Release to Solution of Zinc, Copper and Nickel from Metal-Loaded Sewage Sludges," Environmental Pollution (Series B), Vol 8, pp 85-99.

Alexander, M. 1977. Introduction to Soil Microbiology, John Wiley and Sons Inc., New York.

Bacon, M. P., and Anderson, R. F. 1982. "Distribution of Thorium Isotopes Between Dissolved and Particulate Forms in the Deep Sea," Journal of Geophysical Research, Vol 87, pp 2045-2056.

Balistrieri, L. S., and Murray, J. W. 1983. "Metal-Solid Interactions in the Marine Environment: Estimating the Apparent Equilibrium Binding Constants," Geochimca et Cosmochimica Acta, Vol 47, pp 788-806.

_____. 1986. "The Surface Chemistry of Sediments from the Panama Basin: The Influence of Mn Oxides on Metal Adsorption," Geochimica et Cosmochimica Acta, Vol 50, pp 2235-2243.

Balistrieri, L. S., Brewer, P. G., and Murray, J. W. 1981. "Scavenging Residence Times of Trace Metals and Surface Chemistry of Sinking Particles in the Deep Ocean," Deep Sea Research, Vol 28, pp 101-121.

Ballard, T. M. 1971. "Role of Humic Carrier Substances in DDT Movement Through Forest Soil," Proceedings of the Soil Science Society of America, Vol 35, pp 145-147.

Bird, R. B., Stewart, W. E., and Lightfoot, E. N. 1960. "Transport Phenomena, John Wiley and Sons, New York.

Boehm, P. D., and Quinn, J. G. 1973. "Solubilization of Hydrocarbons by the Dissolved Organic Matter in Sea Water," Geochimica et Cosmochimica Acta, Vol 37, pp 2459-2477.

Braman, R. S., and Foreback, C. C. 1973. "Methylated Forms of Arsenic in the Environment," Science, Vol 182, pp 1247-1249.

Brannon, J. M., Chen, R. L. and Gunnison, D. 1985. "Sediment-Water Interactions and Mineral Cycling in Reservoirs," In: Microbial Processes in Reservoirs, Douglas Gunnison, ed., Dr. W. Junk Publishers, Boston, MA.

Brannon, J. M., Engler, R. M., Rose, J. R., Hunt, P. G., and Smith, I. 1976. "Selective Analytical Partitioning of Sediments to Evaluate Potential Mobility of Chemical Constituents During Dredging and Disposal Operations," Technical Report D-76-7, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Brannon, J. M., Gunnison, D., Averett, D., Martin, J. L, and Chen, R. L. 1989. "Analyses of Impacts of Bottom Sediments from Grand Calumet River and Indiana Harbor Canal on Water Quality," Miscellaneous Paper D-89-1, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Brannon, J. M., Plumb, R. H., Jr., and Smith, I., Jr. 1980. "Long-Term Release of Heavy Metals from Sediments," Contaminants and Sediments, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, Vol 2, pp 221-266.

Brink, R. H. 1983. "Biodegradation of Chlorinated Biphenyls," pp 9-1-9-21, In: A. Leifer, R. H. Brink, G. C. Thom, and K. G. Partymiller, eds., Environmental Transport and Transformation of Polychlorinated Biphenyls, USEPA Report 560/5-83-025, US Environmental Protection Agency, Office of Toxic Substances, Washington, DC.

Brown, J. F., Jr., Bedard, D. L., Brennan, M. J., Carnahan, J. C., Feng, H., and Wagner, R. E. 1987. "Polychlorinated Biphenyl Dechlorination in Aquatic Sediments," Science, Vol 236, pp 709-712.

Cappenberg, T. E. 1974. "Interrelations Between Sulfate-Reducing and Methane-Producing Bacteria in Bottom Deposits of a Freshwater Lake. I. Field Observations," Antonie Van Leevwenhoek, Vol 40, pp 285-295.

Cerniglia, C. E., and Gibson, D. T. 1978. "Metabolism of Naphthalene by Cell Extracts of Cunninghamella elegans," Archives of Biochemistry and Biophysics, Vol 186, pp 121-127.

Cerniglia, C. E., Gibson, D. T., and Van Baalen, C. 1980. "Oxidation of Naphthalene by Cyanobacteria and Microalgae," Journal of General Microbiology, Vol 116, pp 495-500.

Chang, C. C. Y., Davis, J. A., and Kuwabara, J. S. 1987. "A Study of Metal Ion Adsorption at Low Suspended-Solid Concentrations," Estuarine, Coastal and Shelf Science, Vol 24, pp 419-424.

Chen, K. Y., Gupta, S. K., Sycip, A. Z., Lu, J. C. S., Knezenio, M., Choi, W. 1976. "Research Study on the Effect of Dispersion, Settling, and Resedimentation on Migration of Chemical Constituents During Open-Water Disposal of Dredged Material," Contract Report D-76-1, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Corwin, D. L., and Farmer, W. J. 1984. "Nonsingle-Valued Adsorption-Desorption of Bromacil and Diquat by Freshwater Sediments," Environmental Science and Technology, Vol 18, No. 7, pp 507-514.

Crawford, N. H., and Donigan, A. S., Jr. 1973. "Pesticide Transport and Runoff Model for Agricultural Lands," EPA-660/2-74-013, US Environmental Protection Agency, Washington, DC.

Crosby, D. G., and Tucker, R. K. 1971. "Accumulation of DDT by Daphnia magna," Environmental Science and Technology, Vol 5, pp 714-716.

Curl, R. L., and Keoleian, G. A. 1984. "Implicit-Adsorbate Model for Apparent Anomalies with Organic Adsorption on Natural Sediments," Environmental Science and Technology, Vol 18, No. 12, pp 916-922.

Davis, J. A. 1982. "Complexation of Trace Metals by Absorbed Natural Organic Matter," Geochimica et Cosmochimica Acta, Vol 46, pp 2381-2393.

_____. 1984. "Complexation of Trace Metals by Adsorbed Natural Organic Matter," Geochimica et Cosmochimica Acta, Vol 48, pp 679-691.

DeLaune, R. D., Patrick, W. H., Jr., and Casselman, M. E. 1981. "Effect of Sediment pH and Redox Conditions on Degradation of Benzo(a)pyrene," Marine Pollution Bulletin, Vol 12, pp 251-253.

DiToro, D. M., and Horzempa, L. M. 1982. "Reversible and Resistant Components of PCB Adsorption-Desorption: Isotherms," Environmental Science and Technology, Vol 16, No. 9, 594-602.

DiToro, D. M., Horzempa, L. M., Casey, M. M., and Richardson, W. 1982. "Reversible and Resistant Components of PCB Adsorption-Desorption: Adsorbent Concentration Effects," Journal of Great Lakes Research, Vol 8, pp 336-348.

Doran, J. W., and Alexander, M. 1977. Applied and Environmental Microbiology, Vol 33, pp 31-37.

Eadie, B. J., Faust, W., Gardner, W. S., Nalepa, T. 1982. "Polycyclic Aromatic Hydrocarbons in Sediments and Associated Benthos in Lake Erie," Chemosphere, Vol 11, pp 185-191.

Ensley, B. D., Gibson, D. T., and Laborde, A. L. 1982. "Oxidation of Naphthalene by a Multicomponent Enzyme System from Pseudomonas sp. strain NCIB 9816," Journal of Bacteriology, Vol 149, pp 948-954.

Fillos, J., and Molof, A. H. 1972. "The Effect of Benthal Deposits on Oxygen and Nutrient Economy of Flowing Waters," Journal of Water Pollution Control Federation, Vol 44, pp 644-662.

Fleming, R. W., and Alexander, M. 1972. "Dimethylselenide and Dimethyltelluride Formation by a Strain of Penicillium," Applied Microbiology, Vol 24, pp 424-429.

Francis, A. J., Duxbury, J. M., and Alexander, M. 1974. "Evolution of Dimethylselenide from Soils," Applied Microbiology, Vol 28, pp 248-250.

Fulk, R., Gruber, D., and Wullschleger, R. 1975. "Laboratory Study of the Release of Pesticide and PCB Materials to the Water Column During Dredging and Disposal Operations," Contract Report D-75-6, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Furukawa, K. 1982. "Microbial Degradation of Polychlorinated Biphenyls (PCBs)," pp 33-57, In: A. M. Chakrabarty, ed., Biodegradation and Detoxification of Environmental Pollutants, CRC Press, Inc., Boca Raton, FL.

Gambrell, R. P., Khalid, R. A., and Patrick, W. H., Jr. 1980. "Chemical Availability of Mercury, Lead, and Zinc in Mobile Bay Sediment Suspensions as Affected by pH and Oxidation-Reduction Conditions," Environmental Science and Technology, Vol 14, pp 431-436.

Garcia-Miragaya, J., and Page, A. L. 1976. "Influence of Ionic Strength and Inorganic Complex Formation on the Sorption of Trace Amounts of Cd by Montmorillonite," Soil Science Society of America Journal, Vol 40, pp 658-663.

Gaugush, R. F., Gunkel, R. C., Jr., and Kennedy, R. H. "A National Assessment of Water Quality in US Army Corps of Engineers Reservoirs," Technical Report in preparation, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Geankoplis, C. J. 1983. Transport Processes and Unit Operations, Allyn and Bacon, Boston, MA.

Gschwend, P. M., and Wu, S. 1985. "On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants," Environmental Science and Technology, Vol 19, No. 1, pp 90-96.

Gunkel, R. H., Gaugush, R. F., Kennedy, R. H., Saul, G. E., Carroll, J. H., and Gauthey, J. E. 1984. "A Comparative Study of Sediment Quality in Four Reservoirs," Technical Report E-84-2, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Gunnison, D., Patrick, W. H., and Engler, R. M. 1985. "Chemistry and Micro-biology of Newly Flooded Soils: Relationship to Reservoir Water Quality In: D. Gunnison, ed., Microbial Processes in Reservoirs, Dr. W. Junk, Publishers, The Hague, pp 39-57.

Hachlya, K., Ashida, M., Sasaki, M., Kan, H., Inoue, T., and Yasunaga, T. 1979. "Study of the Kinetics of Adsorption-Desorption of Pb2+ on Y-Al2O3 Sur-face by Means of Relaxation Techniques," Journal of Physical Chemistry, Vol 83, pp 1866-1871.

Hallett, D. J., and Brecher, R. W. 1984. "Cycling of Polynuclear Aromatic Hydrocarbons in the Great Lakes Ecosystem," pp 213-237, In: J. O. Nriagu and M. S. Simmons, eds., Toxic Contaminants in the Great Lakes, John Wiley and Sons, Inc., New York.

Hassett, J. P., and Anderson, M. A. 1979. "Association of Hydrophobic Organic Compounds with Dissolved Organic Matter in Aquatic Systems," Environ-mental Science and Technology, Vol 13, pp 1526-1529.

_____. 1982. "Effects of Dissolved Organic Matter on Adsorption of Hydrophobic Organic Compounds by River- and Sewage-Borne Particles," Water Research, Vol 16, pp 681-686.

Hayes, K. F., and Leckie, J. O. 1986. "Kinetic Studies of Ion Adsorption at the Goethite/Water Interface Using the Pressure Jump Relaxation Technique," In: Surface Processes in Aqueous Geochemistry, J. A. Davis and K. F. Hayes, eds., American Chemical Society Symposium Series, Washington, D. C.

Hill, D. O., Myers, T. E., and Brannon, J. M. 1988. "Development and Appli-cation of Techniques for Predicting Leachate Quality in Confined Disposal Facilities: Background and Theory," Miscellaneous Paper D-88-1, US Army Engi-neer Waterways Experiment Station, Vicksburg, MS.

Holm, T. R., Anderson, M. A., Stanforth, R. R., and Iverson, D. G. 1980. "The Influence of Adsorption on the Rates of Microbial Degradation of Arsenic Species in Sediments," Limnology and Oceanography, Vol 25, pp 23-30.

Houle, M. J., and Long, D. E. 1980. "Interpreting Results from Serial Batch Extraction Tests of Water and Soils," Disposal of Hazardous Waste; Proceedings of the Sixth Annual Research Symposium, EPA-600/9-80-010, US Environmental Protection Agency, Cincinnati, OH, pp 60-81.

Isaacson, P. J., and Frink, C. R. 1984. "Nonreversible Sorption of Phenolic Compounds by Sediment Fractions: The Role of Sediment Organic Matter," Envi-ronmental Science and Technology, Vol 18, No. 1, pp 43-48.

Jannasch, H. W., Honeyman, B. D., Balistriere, L. S., and Murray, J. W. 1988. "Kinetics of Trace Element Uptake by Marine Particles," Geochimica et Cosmo-chimica Acta, Vol 53, pp 567-577.

Karickhoff, S. W. 1984. "Organic Pollutant Sorption in Aquatic Systems," Journal of Hydraulic Engineering, Vol 110, pp 107-735.

Karickhoff, S. W. 1980. "Sorption Kinetics of Hydrophobic Pollutants in Natural Sediments," In: R. A. Baker, ed, Contaminants and Sediments, Vol II, Ann Arbor Science Publishers, Ann Arbor, MI, pp 193-205.

Karickhoff, S. W., and Morris, K. R. 1985. "Sorption Dynamics of Hydrophobic Pollutants in Sediment Suspensions," Environmental Toxicology and Chemistry, Vol 4, pp 469-479.

Kennedy, R. H., Thornton, K. W., and Ford, D. E. 1985. "Characterization of the Reservoir Ecosystem," pp 27-38, In: D. Gunnison, ed., Microbial Processes in Reservoirs (Developments in Hydrobiology), D. W. Junk, Publishers, Dordrecht.

Khalid, R. A., Gambrell, R. P., Taylor, B. A., and Patrick, W. H., Jr. 1983. "Literature Survey of Reservoir Contaminant Problems," Technical Report E-83-13, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Khan, S. U. 1978a. "Kinetics of Hydrolysis of Atrazine in Aqueous Fulvic Acid Solution," Pesticide Science, Vol 9, pp 39-43.

_____. 1978b. "The Interaction of Organic Matter with Pesticides," pp 137-166, In: M. Schnitzer and S. U. Khan, eds., Soil Organic Matter, Elsevier Scientific Publishing Company.

Kiyohara, H., and Nagao, K. 1978. "The Catabolism of Phenanthrene and Naphthalene by Bacteria," Journal of General Microbiology, Vol 105, pp 69-75.

LaFlamme, B. D., and Murray, J. W. 1987. "Solid/Solution Interaction: The Effect of Carbonate Alkalinity on Adsorbed Throium," Geochimica et Cosmochimica Acta, Vol 51, pp 245-250.

Landrum, P. F., Nihart, S. R., Eadie, B. J., and Gardner, W. S. 1984. "Reverse-Phase Separation Method for Determining Pollutant Binding to Aldrich Humic Acid and Dissolved Organic Carbon of Natural Waters," Environmental Science and Technology, Vol 18, pp 187-192.

Lerman, A. 1979. Geochemical Processes Water and Sediment Environments, John Wiley and Sons, New York.

Leversee, G. J., Giesy, J. P., Landrum, P. F., Bartell, S., Gerould, S., Bruno, M., Spacie, A., Bowling, J., Haddock, J., and Fannin, T. 1981. "Disposition of Benzo(a)pyrene in Aquatic Systems Components: "Periphyton, Chironomids, Daphnia, Fish," In: M. Cooke and A. Dennis, eds., Polynuclear Aromatic Hydrocarbons, Batelle Press, Columbus, OH, pp 357-366.

Leversee, G. J., Landrum, P. F., Giesy, J. P., and Fannin, T. 1983. "Humic Acids Reduce Bioaccumulation of Some Polycyclic Aromatic Hydrocarbons," Canadian Journal of Fisheries and Aquatic Science, Vol 40, pp 63-69.

Li, G. C. and Felbeck, G. T., Jr. 1972a. "Atrazine Hydrolysis Catalyzed by Humic Acids," Soil Science, Vol 114, pp 201-209.

_____. 1972b. "Study of the Mechanism of Atrazine Adsorption by Humic Acid from Much Soil," Soil Science, Vol 113, pp 140-148.

Li, Y.-H. 1981. "Ultimate Removal Mechanisms of Elements from the Ocean," Geochimica et Cosmochimica Acta, Vol 45, pp 1659-1664.

Li, Y.-H., Burkhardt, L., Buchholtz, M., O'Hara, P., and Santschi, P. H. 1984. "Partition of Radiotracers Between Suspended Particles and Seawater," Geochimica et Cosmochimica Acta, Vol 48, pp 2011-2019.

Loganathan, R. G., Burau, R. G., and Fuerstenau, D. W. 1977. "Influence of pH on the Sorption of Co2+, Zn2+, and Ca2+ by a Hydrous Manganese Oxide," Soil Science Society of America Journal, Vol 41, pp 57-62.

Mantoura, R. F. C., Dickson, A., and Riley, J. P. 1978. "The Complexation of Trace Metals with Humic Materials in Natural Waters," Estuarine and Coastal Marine Science, Vol 6, pp 387-409.

Mathur, S. P., and Morely, H. V. 1978. "Incorporation of Methoxychlor-14C in Model Humic Acids Prepared from Hydroquinone," Bulletin of Environmental Contamination and Toxicology, Vol 20, pp 268-274.

Matsuda, K., and Schnitzer, M. 1973. "Reactions Between Fulvic Acid, a Soil Humic Material, and Dialkyl Phthalates," Bulletin of Environmental Contamination and Toxicology, Vol 6, pp 200-204.

McElroy, A. E., Tripp, B. W., Farrington, J. W., and Teal, J. M. 1987. "Biogeochemistry of Benz(a)anthracene at the Sediment-Water Interface," Chemosphere, Vol 16, pp 2429-2440.

Mihelcic, J. R., and Luthy, R. G. 1988a. "Degradation of Polycyclic Aromatic Hydrocarbon Compounds Under Various Redox Conditions in Soil-Water Systems," Applied and Evironmental Microbiology, Vol 54, pp 1182-1187.

_____. 1988b. "Microbial Degradation of Acenaphthene and Naphthalene Under Denitrification Conditions in Soil-Water Systems," Applied and Environmental Microbiology, Vol 54, pp 1188-1198.

Mills, G. L., Hanson, A. K., Jr., Quinn, J. G., Lammela, W. R., and Chasteen, N. D. 1982. "Chemical Studies of Copper-Organic Complexes Isolated from Estuarine Waters Using C-18 Reverse-Phase Liquid Chromatography," Marine Chemistry, Vol 11, pp 355-377.

Mortimer, C. H. 1941. "The Exchange of Dissolved Substances Between Mud and Water in Lakes," Journal of Ecology, Vol 29, Parts I and II, pp 280-329.

_____. 1942. "The Exchange of Dissolved Substances Between Mud and Water in Lakes," Journal of Ecology, Vol 30, Parts III and IV, pp 147-201.

Mustafa, M. A., and Gamer, Y. 1972. "Adsorption and Desorption of Diuron as a Function of Soil Properties," Soil Science Society of America Proceedings, Vol 36, pp 561-565.

Neal, R. H., Sposito, G., Holtzclaw, K. M., and Traina, S. J. 1987. "Selenite Adsorption on Alluvial Soils: II. Solution Composition Effects," Soil Science Society of America Journal, Vol 51, pp 1165-1169.

Neely, W. B., Branson, D. R., and Blau, G. E. 1974. "Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish," Environmental Science and Technology, Vol 8, pp 1113-1115.

Newton, P. P., and Liss, P. S. 1987. "Positively Charged Suspended Particles: Studies in an Iron-Rich River and Its Estuary," Limnology and Oceanography, Vol 32, pp 1267-1276.

Novick, N. J., and Alexander, M. 1965. "Cometabolism of Low Concentrations of Propachlor, Alachlor, and Cycloate in Sewage and Lake Water," Applied and Environmental Microbiology, Vol 49, pp 737-743.

Nyffeler, U. P., Li, Y.-H., and Santschi, P. H. 1984. "A Kinetic Approach to Describe Trace-Element Distribution Between Particles and Solution in Natural Systems," Geochimica et Cosmochimica Acta, Vol 48, pp 1513-1522.

Nyffeler, U. P., Santschi, P. H., and Li, Y.-H. 1986. "The Influence of Scavenging Kinetics to Modeling of Sediment-Water Interactions in Natural Waters," Limnology and Oceanography, Vol 31, pp 277-292.

O'Connor, D. J. 1988a. "Models of Sorptive Toxic Substances in Freshwater Systems. I: Basic Equations," Journal of Environmental Engineering, Vol 114, pp 507-532.

_____. 1988b. "Models of Sorptive Toxic Substances in Freshwater Systems. II: Lakes and Reservoirs," Journal of Environmental Engineering, Vol 114, pp 533-551.

_____. 1988c. "Models of Sorptive Toxic Substances in Freshwater Systems. III: Streams and Rivers," Journal of Environmental Engineering, Vol 114, pp 552-574.

O'Connor, D. J., and Connolly, J. P. 1980. "The Effect of Concentration of Adsorbing Solids on the Partition Coefficient," Water Research, Vol 14, pp 1517-1523.

Ogner, G., and Schnitzer, M. 1970a. "Humic Substances: Fulvic Acid-Dialkyl Phthalate Complexes and Their Role in Pollution," Science, Vol 170, pp 317-318.

_____. 1970b. "The Occurrence of Alkenes in Fulvic Acid, a Soil Humic Fraction," Geochimica Cosmochimica Acta, Vol 34, pp 921-928.

Paris, D. F., Wolfe, N. L., and Steen, W. C. 1982. "Structure-Activity Relationships in Microbial Transformation of Phenols," Applied and Environmental Microbiology, Vol 44, pp 153-158.

Perdue, E. M. 1983. "Association of Organic Pollutants with Humic Substances: Partitioning Equilibria and Hydrolysis Kinetics," pp 441-460, In: R. F. Christman and E. Gjessing, eds., Aquatic and Terrestrial Humic Materials, Ann Arbor Science, Ann Arbor, MI.

_____. 1985. "Acidic Functional Groups of Humic Substances, pp 493-526, In: G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. McCarthy, eds., Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization, John Wiley and Sons, Inc., New York.

Perdue, E. M., and Wolf, N. L. 1984. "Prediction of Buffer Catalysis in Field and Laboratory Studies of Pollutant Hydrolysis Reactions," Environmental Science and Technology, Vol 17, pp 635-642.

Ponnamperuma, F. N. 1972. "The Chemistry of Submerged Soils," Advances in Agronomy, Vol 24, pp 29-88.

Pritchard, P. H., Monti, C. A., O'Neill, E. J., Connolly, J. P., and Ahern, D. G. 1986. "Movement of Kepone (Chlordecane) Across an Undisturbed Sediment-Water Interface in Laboratory Systems," Environmental Toxicology and Chemistry, Vol 5, pp 647-657.

Rao, P. S. C., et al. 1979. "Evaluation of Conceptual Models for Describing Nonequilibrium Adsorption-Desorption of Pesticides During Steady-Flow in Soils," Soil Science Society of America Journal, Vol 43, pp 22-28.

Reuber, B., Mackay, D., Paterson, S., and Stokes, P. 1987. "A Discussion of Chemical Equilibria and Transport at the Sediment-Water Interface," Environmental Toxicology and Chemistry, Vol 6, pp 731-739

Ross, F., Nriagu, J. O., and Wong, H. K. 1983. "Particulate Flux at the Bottom of Lake Ontario," Chemosphere, Vol 12, pp 1345-1354.

Ross, R. D., and Crosby, D. G. 1975. "Photoxidation of Aldrin in Water", Chemosphere, Vol 4, pp 277-282.

Ryding, S. O. 1985. "Chemical and Microbiological Processes as Regulators of the Exchange of Substances Between Sediments and Water in Shallow Eutrophic Lakes," Internationale Revue Gesamten Hydrobiologie, Vol 70, pp 657-702.

Santschi, P. H. 1984. "Particle Flux and Trace Metal Residence Time in Natural Waters," Limnology and Oceanography, Vol 29, pp 1100-1108.

Santschi, P. H., Nyffeler, U. H., Anderson, R. F., Schiff, S. L., and O'Hara, P. 1986. "Response of Radioactive Trace Metals to Acid-Base Titrations in Controlled Experimental Ecosystems: Evaluation of Transport Parameters for Application to Whole-Lake Radiotracer Experiments," Canadian Journal of Fish Aquatic Science, Vol 43, pp 60-77.

Schmidt, S. K., and Alexander, M. 1985. "Effects of Dissolved Organic Carbon and Second Substrates on the Biodegradation of Organic Compounds at Low Concentrations," Applied and Environmental Microbiology, Vol 49, pp 833-837.

Schnitzer, M., and Khan, S. U. 1972. "Humic Substances in the Environment," Marcel Dekker, Inc., New York.

Schnoor, G. L. 1981. "Fate and Transport of Dieldrin in Coralville Reservoir: Residues in Fish and Water Following a Pesticide Ban," Science, Vol 211, pp 840-842.

_____. 1985. "Modeling Chemical Transport in Lakes, Rivers, and Estuarine Systems," pp 52-73, In: W. B. Neely and G. E. Blaw, eds., Environmental Exposure for Chemicals, Vol 2, CRC Press, Boca Raton, FL.

Schocken, M. J., and Gibson, P. T. 1984. "Bacterial Oxidation of the Polycyclic Aromatic Hydrocarbons Acenaphtene and Acenaphthylene," Applied and Environmental Microbiology, Vol 48, pp 10-16.

Shuman, L. M. 1977. "Adsorption of Zn by Fe and Al Hydrous Oxides as Influenced by Aging and pH," Soil Science Society of America Journal, Vol 41, pp 703-706.

Southworth, G. R., Beauchamp, J. J., and Schneider, P. S. 1978. "Bioaccumulation Potential and Acute Toxicity of Synthetic Fuels Effluents in Fresh Water Biota: Azaarenes," Enviromental Science and Technology, Vol 12, pp 1062-1066.

Staples, C. A., and Geiselmann, S. J. 1988. "Influence of Sorbent Concentration on Sorption of Kepone to Solids," Environmental Toxicology and Chemistry, Vol 7, pp 139-142.

Stumm, W., Huang, C. P., and Jenkins, S. R. 1970. "Specific Chemical Interactions Affecting the Stability of Dispersed Systems," Croatica Chemica Acta, Vol 42, pp 223-245.

Summers, A. O., and Silver, S. 1978. "Microbial Transformations of Metals," Annual Review of Microbiology, Vol 32, pp 637-672.

Sundby, B., Anderson, L. G., Hall, P. O., Inerfeldt, A., Van Der Loeff, M. M. R., and Westerlund, S. F. G. 1986. "The Effect of Oxygen on Release and Uptake of Cobalt, Manganese, Iron and Phosphate at the Sediment-Water Interface," Geochimica et Cosmochimica Acta, Vol 50, pp 1281-1288.

Thibodeaux, L. J. 1979. Chemodynamics, John Wiley and Sons, Inc., New York.

Thornton, K. W., Kennedy, R. H., Carroll, J. H., Gunkel, R. C., and Ashley, S. 1981. "Reservoir Sedimentation and Water Quality--An Heuristic Model," In: H. Stefan, ed., Proceedings of the Symposium on Surface Water Impoundments, American Society of Civil Engineers, Minneapolis, MN, Vol I, pp 654-661.

Trefry, J. H., and Metz, S. 1984. "Selective Leaching of Trace Metals from Sediments as a Function of pH," Analytical Chemistry, Vol 56, pp 745-749.

Voice, T. C., Rice, C. P., and Weber, W. J., Jr. 1983. "Effect of Solids Concentration on the Sorptive Partitioning of Hydrophobic Pollutants in Aquatic Systems," Environmental Science and Technology, Vol 17, No. 9, pp 513-518.

Weber, W. J., Jr. 1972. Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York.

Wershaw, R. L., Burcar, P. J., and Goldberg, M. C. 1969. "Interaction of Pesticides with Natural Organic Material," Environmental Science and Technology, Vol 3, pp 271-273.

Westerlund, S. F. G., et al. 1986. "Benthic Fluxes of Cadmium, Copper, Nickel, Zinc and Lead in the Coastal Environment," Geochimica et Cosmochimica Acta, Vol 50, pp 1289-1296.

Whitfield, M., and Turner, D. R. 1979. "Water-Rock Partition Coefficients and the Composition of Seawater and River Water," Nature, Vol 278, pp 132-137.

Witkowski, P. J., Smith, J. A., Fusillo, T. V., and Chiou, C. J. 1987. "A Review of Surface-Water Sediment Fractions and Their Interactions with Persistent Man-Made Organic Compounds," Circular 993, US Geological Survey, Denver, CO.

Wu, S., and Gschwend, P. M. 1986. "Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils," Environmental Science and Technology, Vol 20, No. 7, pp 717-725.

Yoshida, T. 1975. "Microbial Metabolism of Flooded Soils," In: E. A. Paul and A. D. McLaren, eds., Soil Biochemistry, Marcel Dekker, Inc., Vol 3, pp 83-122.

Zepp, R. G., Baughman, G. L., and Schlotzhauer, P. F. 1981a. "Comparison of Photochemical Behavior of Various Humic Substances in Water. I. Sunlight Induced Reactions of Aquatic Pollutants Photosensitized by Humic Substances," Chemosphere, Vol 10, pp 109-117.

_____. 1981b. "Comparison of Photochemical Behavior of Various Humic Substances in Water. II. Photosenitized Oxygenations," Chemosphere, Vol 10, pp 119-126.

Zepp, R. G., Wolfe, N. L., Baughman, G. L., and Gordon, J. A. 1975. "Chemical and Photochemical Alteration of 2,4-D Esters in the Aquatic Environment," Environmental Quality and Safety, Supplement, Vol 3, pp 313-318.

Zepp, R. G., Wolfe, N. L., Baughman, G. L., and Hollis, R. C. 1977. "Singlet Oxygen in Natural Waters," Nature, Vol 267, pp 421-423.